PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference O.Z. 6205-WO	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/EP2004/050327	International filing date *(day/month/year)* 18.03.2004	Priority date *(day/month/year)* 14.05.2003
International Patent Classification (IPC) or national classification and IPC C08J3/22, C08L83/04, C08L83/06, C08L83/08, C08L101/00		
Applicant DEGUSSA AG		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 8 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☒	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
21.10.2004	29.09.2005
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Lentz, J.C. Telephone No. +31 70 340-2130

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/050327

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1, 2, 9-18	as originally filed
3-8	filed with the demand

Claims, Numbers

1-11	filed with the demand

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-11
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-11
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V.

1 The following documents are referred to in this communication:
D1 : US 2001/018486 A1 (LICHTENHAN ET AL) 30 August 2001 (2001-08-30)
D2 : US 2003/018109 A1 (HSIAO ET AL) 23 January 2003 (2003-01-23)
D3 : WO 03042292, published 22 May 2003.
D4: US20030050408

The cited documents describe compsitions comprising thermoplastic material and polyhedral oligomeric silicon-oxygen cluster units (polyhedral oligomeric silsesquioxane, 'POSS'.) falling under the definition of the silicon compound of present claim 1.

D1 discloses a method comprising the addition of polyhedral oligomeric silsesquioxane to thermoplastic organic polymers such as polystyrene, polyesters etc, see page 1 [0014] and claims 1 and 8. The POSS in D1 can be added as monomer, polymer or copolymer.

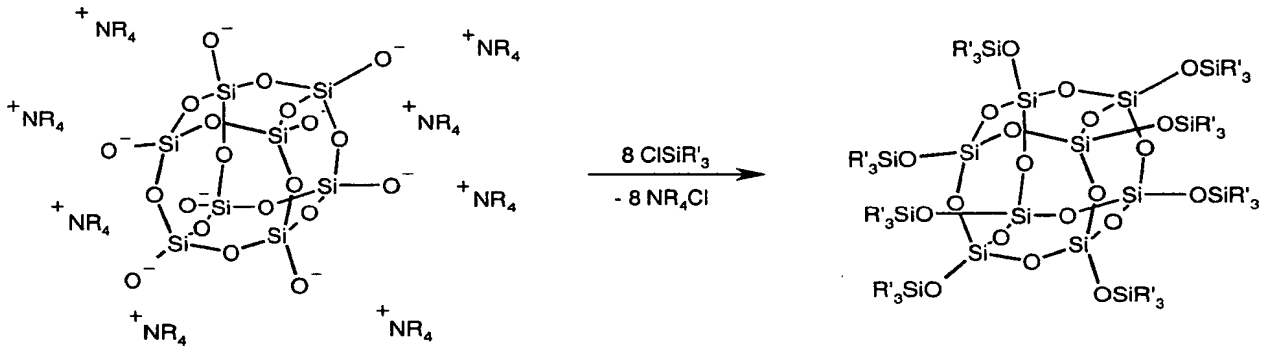
If the composition of D1 falls under present claim 1, it should also be suitable for improving the surface properties of thermoplastics. Present claim 1 therefore lacks novelty in view of D1. Claims 2-11 do not seem to contain any further technical features that could help to solve a technical problem in an unexpected way. The patentability of these claims thus depend on the patentabiltiy of the main claim.

A new main claim directed to the use of said composition would however seem allowable.

Conc. claim 1, it seems that the thermoplastic ingredient of the composition is mentioned twice, first on line 2 and secondly on the two last lines of claim 1. It is suggested to amend the wording on line 2 to "comprising from 40% to 90% of a thermoplastic carrier material selected from..."
Furthermore, the definition of substituent X is unclear in that for example 'oxy' is not a clear and well-defined group but a linking group/atom which is also part of other groups listed under X. This objection also relates to groups such as silyl, siloxy,alkylsilyl,alkoxysilyl, alkylsiloxy, ester.

Claims 9,10 and 11 are characterized by an effect to be achieved, i.e. desiderata, rather than by a technical descriptive feature which is not allowable.

to a further oxygen atom, which in turn is substituted further. Oligomeric spherosilicates can be prepared by silylating suitable silicate precursors (D. Hoebbel, W. Wieker, Z. Anorg. Allg. Chem. **384** (1971), 43-52; P. A. Agaskar, Colloids Surf. **63** (1992), 131-8; P. G. Harrison, R. Kannengiesser, C. J. Hall, J. Main Group Met. Chem. **20** (1997), 137-141; R. Weidner, Zeller, B. Deubzer, V. Frey, Ger. Offen. (1990), DE 38 37 397). For example, the spherosilicate with the structure **2** can be synthesized from the silicate precursor of the structure **1**, which in turn is obtainable from the reaction of $Si(OEt)_4$ with choline silicate or by the reaction of waste products from the harvesting of rice with tetramethylammonium hydroxide (R. M. Laine, I. Hasegawa, C. Brick, J. Kampf, Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001, MTLS-018).



1 2

The silasequioxanes and the spherosilicates are both thermally stable at temperatures up to several hundred degrees Celsius.

The present invention provides a transparent masterbatch for improving the surface properties of thermoplastics comprising at least one polymer selected from polyester, copolyester, copolyamide, cyclic olefin copolymer (COC), polymethyl methacrylate, polyphenylene ether, polyurethane, polysiloxane, polysilane, polytetrafluoroethylene, polyoxymethylene, polyvinyl chloride, vinyl chloride copolymer, polystyrene, acrylonitrile-butadiene-styrene copolymers (ABS polymers) or styrene-acrylonitrile copolymers (SAN polymers), said masterbatch

containing from 10% to 60% by weight of polyhedral oligomeric silicon-oxygen cluster units in accordance with the formula

$$[(R_aX_bSiO_{1.5})_m (R_cX_dSiO)_n (R_eX_fSi_2O_{2.5})_o (R_gX_hSi_2O_2)_p]$$

where:

a, b, c = 0-1; d = 1-2; e, f, g = 0-3; h = 1-4; m+n+o+p ≥ 4; a+b = 1; c+d = 2; e+f = 3 and g+h = 4;

R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl group or polymer unit, each substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units attached via a polymer unit or a bridging unit,

X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type **R** containing at least one such group of type **X**,

the substituents of type **R** being identical or different and the substituents of type **X** being identical or different and from 40% to 90% by weight of a thermoplastic carrier material.

The present invention also provides a process for preparing a transparent thermoplastic, which comprises mixing one part by weight of the masterbatch of the invention into from 3 to 11 parts by weight of a thermoplastic polymer mechanically without solvent at a temperature of at least 50°C.

The invention further provides a transparent thermoplastic prepared by the process of the invention, wherein the concentration of the polyhedral oligomeric silicon-oxygen cluster units in the polymer composition is not more than 5% by weight.

The masterbatch of the invention has the advantage over the prior art that the polyhedral oligomeric silicon-oxygen cluster units are present in extremely finely divided form in the thermoplastic carrier material; in other words, the particle size of the polyhedral oligomeric silicon-oxygen clusters is well below the wavelength of visible light. The fillers added in accordance with the prior art to increase the hardness and scratch resistance, by contrast, are inorganic in nature and have a particle size which is above the wavelength of visible light.

The masterbatch of the invention is therefore highly suitable for the preparation of transparent thermoplastics. The plastics prepared by means of the masterbatch of the invention, furthermore, display a transparency, provided that the plastic was already transparent before the masterbatch was added. As well as the positive aspect in relation to the transparency, it is also possible for the addition of the masterbatch of the invention to raise the scratch resistance as compared with the plain thermoplastic. A further advantage of the masterbatch of the invention is the increase in the glass transition temperature of the thermoplastic. Another advantageous feature of the masterbatch of the invention is that the tactility of the thermoplastics prepared from it is enhanced. Moreover, the masterbatch of the invention features good processing properties. Use of the masterbatch of the invention results not only in an increase in the scratch resistance of the plastic, with retention of the light transmittance, but also in an increase in the thermal stability and in an increase in the electrical resistance. In contradistinction to many conventional additives, it is possible, by way of the substituents of the polyhedral oligomeric silicon-oxygen cluster units, to control the behavior of the masterbatch of the invention and hence also to influence the properties of the plastic which results from it. The physical and chemical properties can therefore be tailored. The polarity can be set by way of the substituents of type **R** and **X** on the polyhedral oligomeric silicon-oxygen cluster units. By way of the different structure and polarity of these substituents it is possible to control whether the polyhedral oligomeric silicon-oxygen cluster units will have a more organic or more inorganic character. Depending on structure, the polyhedral masterbatches of the invention can have great thermal stability.

The transparent masterbatch of the invention for improving the surface properties of thermoplastics inventively contains from 10% to 60% by weight of polyhedral oligomeric silicon-oxygen cluster units in accordance with the formula

$$[(R_aX_bSiO_{1.5})_m\ (R_cX_dSiO)_n\ (R_eX_fSi_2O_{2.5})_o\ (R_gX_hSi_2O_2)_p]$$

where:

a, b, c = 0-1; d = 1-2; e, f, g = 0-3; h = 1-4; $m+n+o+p \geq 4$; $a+b = 1$; $c+d = 2$; $e+f = 3$ and $g+h = 4$;

R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl group or polymer unit, each substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units attached via a polymer unit or a bridging unit,
X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type **R** containing at least one such group of type **X**,
the substituents of type **R** being identical or different and the substituents of type **X** being identical or different and from 40% to 90% by weight of a thermoplastic carrier material.

The masterbatch of the invention contains preferably from 20 to 50% by weight of polyhedral oligomeric silicon-oxygen cluster units and from 50% to 80% by weight of the thermoplastic carrier material, more preferably from 20% to 40% by weight of polyhedral oligomeric silicon-oxygen cluster units and from 60% to 80% by weight of the thermoplastic carrier material.

Preferably the thermoplastic carrier material comprises at least one polymer selected from polyester, copolyester, polymethyl methacrylate or copolyamides.

In one particular embodiment of the masterbatch of the invention the thermoplastic carrier material comprises further additives, examples being heat stabilizers and light stabilizers, optical brighteners, antistats, lubricants, antiblocking agents, fillers, dyes or pigments – depending on the subsequent use of the plastic.

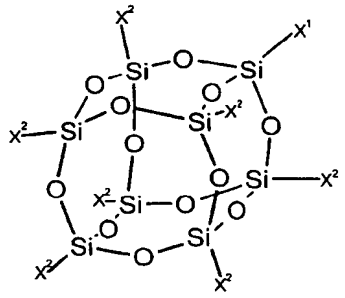
The polyhedral oligomeric silicon-oxygen clusters of the masterbatch of the invention preferably contain substituents of type **X**, which represent an amino, hydroxy, carboxy, isocyanate, epoxy, polyether, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy or alkoxysilylalkyl group. The polyhedral oligomeric silicon-oxygen clusters preferably contain a substituent of type **X** selected from alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, alkoxysilylalkyl, amino, hydroxy, isocyanate or epoxy group. With particular preference, however, the substituent of the type **X** or of the type **R** contains a vinylic group.

On the basis of their molecular character the polyhedral oligomeric silicon-oxygen clusters of

the masterbatch of the invention possess a uniform and defined molecular weight. In one particular embodiment of the masterbatch of the invention the polyhedral oligomeric silicon-oxygen cluster unit has a molecular weight of preferably at least 400 g/mol, more preferably from 400 to 2500 g/mol, and with particular preference from 600 to 1500 g/mol.

The molecular size of the polyhedral oligomeric silicon-oxygen clusters of the masterbatch of the invention can be increased by joining two or more polyhedral oligomeric silicon-oxygen cluster units, functionalized with two reactive groups **X**, by means of condensation by way, for example, of a spacer and/or of the functional groups of the substituent of type **X**. Enlargement can also be achieved by means of homopolymerization or copolymerization. The masterbatch of the invention comprises polyhedral oligomeric silicon-oxygen clusters which preferably have a molecular size of not more than 100 nm, more preferably not more than 50 nm, very preferably not more than 30 nm, and with particular preference not more than 20 nm.

It can be advantageous for the masterbatch of the invention to comprise polyhedral oligomeric silicon-oxygen cluster unit based on the structure **3**



3

where $\mathbf{X^1}$ = substituent of type **X** or of type **–O-SiX$_3$**, $\mathbf{X^2}$ = substituent of type **X**, of type **-O-SiX$_3$**, of type **R**, of type **–O-SiX$_2$R**, of type **–O-SiXR$_2$** or of type **–O-SiR$_3$**,

R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl or cycloalkynyl group or polymer unit, each substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units, attached via a polymer unit or a

bridging unit,

X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type **R** containing at least one such group of type **X**.

The polyhedral oligomeric silicon-oxygen cluster unit of the masterbatch of the invention is preferably functionalized; in particular, the polyhedral oligomeric silicon-oxygen cluster unit represents a spherosilicate unit in accordance with the formula

$[(R_eX_fSi_2O_{2.5})_o\ (R_gX_hSi_2O_2)_p]$ where e, f, g = 0-3; h = 1-4; o+p ≥ 4; e+f = 3 and g+h = 4,

but preferably a functionalized oligomeric spherosilicate unit, but more preferably a silasesquioxane unit in accordance with the formula

$[(R_aX_bSiO_{1.5})_m\ (R_cX_dSiO)_n]$ where a, b, c = 0-1; d = 1-2; m+n ≥ 4; a+b = 1; c+d = 2,

but very preferably a functionalized oligomeric silasesquioxane unit. Very particular preference is given to nucleating agents based on an oligomeric silasesquioxane unit in accordance with structure **4**, **5** or **6**,

What is claimed is:

1. A transparent masterbatch for improving the surface properties of thermoplastics comprising at least one polymer selected from polyester, copolyester, copolyamide, cyclic olefin copolymer (COC), polymethyl methacrylate, polyphenylene ether, polyurethane, polysiloxane, polysilane, polytetrafluoroethylene, polyoxymethylene, polyvinyl chloride, vinyl chloride copolymer, polystyrene, crylonitrile-butadiene-styrene copolymers (ABS polymers) or styrene-acrylonitrile copolymers (SAN polymers), said masterbatch containing from 10% to 60% by weight of polyhedral oligomeric silicon-oxygen cluster units in accordance with the formula

$$[(R_aX_bSiO_{1.5})_m\ (R_cX_dSiO)_n\ (R_eX_fSi_2O_{2.5})_o\ (R_gX_hSi_2O_2)_p]$$

where:

a, b, c = 0-1; d = 1-2; e, f, g = 0-3; h = 1-4; m+n+o+p ≥ 4; a+b = 1; c+d = 2; e+f = 3 and g+h = 4;

R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl group or polymer unit, each substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units attached via a polymer unit or a bridging unit,

X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type **R** containing at least one such group of type **X**,

the substituents of type **R** being identical or different and the substituents of type **X** being identical or different and containing from 40% to 90% by weight of a thermoplastic carrier material.

2. A masterbatch as claimed in claim 1, wherein the silicon-oxygen cluster unit comprises not more than 1 substitutent of type **X**.

3. A masterbatch as claimed in claim 1 or 2, wherein the thermoplastic carrier material comprises further additives.

4. A masterbatch as claimed in at least one of claims 1 to 3, wherein the thermoplastic carrier material comprises at least one polymer selected from polyester, copolyester, polymethyl methacrylate or copolyamides.

5. A masterbatch as claimed in at least one of claims 1 to 4, containing from 20 to 50% by weight of polyhedral oligomeric silicon-oxygen cluster units and from 50 to 80% by weight of the thermoplastic carrier material.

6. A masterbatch as claimed in at least one of claims 1 to 5, wherein the polyhedral oligomeric silicon-oxygen cluster unit has a molecular size of not more than 100 nm.

7. A process for preparing a transparent thermoplastic, which comprises mixing one part by weight of the masterbatch of at least one of claims 1 to 6 into from 3 to 11 parts by weight of a further thermoplastic polymer mechanically without solvent at a temperature of at least 50°C.

8. A transparent thermoplastic prepared by a process as claimed in claim 7, wherein the concentration of the polyhedral oligomeric silicon-oxygen cluster units is not more than 5% by weight.

9. A transparent thermoplastic as claimed in claim 8, whose scratch resistance is higher than that of the plain thermoplastic.

10. A transparent thermoplastic as claimed in claim 8 or 9, whose glass transition temperature is at least 5% higher than that of the plain thermoplastic.

11. A transparent thermoplastic as claimed in at least one of claims 8 to 10, having a soft, velvety, "velour like" tactility.